Electronic Supplementary Material (ESI) for RSC Advances.

Accessing α-aminophosphonates using solvate ionic liquids.

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SUPPLEMENTARY INFORMATION

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General Experimental

All ^{1}H and ^{13}C NMR spectra were recorded on a Jeol JNM-EX 270 MHz, Jeol JNM-EX 400 MHz or Bruker AVANCE III 500 MHz standard bore (solution) as indicated. Samples were dissolved in deuterated chloroform ($CDCl_3$) with the residual solvent peak used as an internal reference ($CDCl_3$ – δ H 7.26 ppm). Proton spectra are reported as follows: chemical shift δ (ppm), (integral, multiplicity (s = singlet, br s = broad singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet), coupling constant J (Hz), assignment).

Thin Layer Chromatography (TLC) was performed using aluminium-backed Merck TLC Silica gel 60 F254 plates, and samples were visualised using 254 nm ultraviolet (UV) light, and potassium permanganate/potassium carbonate oxidising dip (1:1:100 $KMnO_4$:K_2CO_3:H_2O w/w).

Column Chromatography was performed using silica gel 60 (70-230 mesh). All solvents used were AR grade. Specialist reagents were obtained from Sigma-Aldrich Chemical Company and used without further purification. Petroleum spirits refers to the fraction boiling between 40-60 °C.

Note that all compounds synthesised have been previously synthesised, thus only ^{1}H NMR is provided here for comparison.

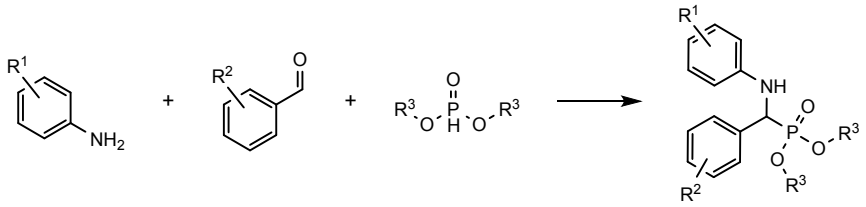
Experimental Section

Preparation of Solvate Ionic Liquids (G3TFSI and G4TFSI)

Lithium bis(trifluromethanesulfonyl)amide (63.53 g, 0.22 mol) was added to tri-/tetra-ethylene glycol dimethyl ether (0.22 mol) in a round bottom flask and heated to 60 °C under nitrogen atmosphere overnight. The resulting product is a viscous, amber liquid. Some removal of adventitious water may be required (if the liquid is colourless); achieved through heating to 120 °C under high vacuum for up to 4 hours. This process can be loosely assessed to be complete when the liquid goes from colourless to amber.

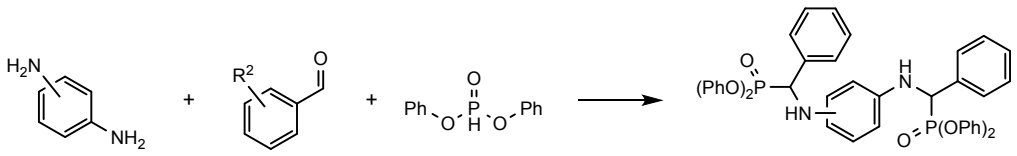
General preparation of α-aminophosphonates

Monomers



A round bottom flask was charged with aldehyde (1.00 mmol), which was dissolved in either $[G3(Li)]^+$ TFSI or $[G4(Li)]^+$ TFSI (0.5 mL). Aniline (1.00 mmol) was then added, before the addition of diphenyl phosphite (0.230 mL, 1.20 mmol) and stirred at room temperature for the given time period. Diethyl ether (10 mL) was added at the conclusion of the reaction, before the addition of deionised water (10 mL) causing a fine precipitate to form. The removal of diethyl ether under reduced pressure afforded a suspension of precipitate in the aqueous phase, which was then filtered washing with excess water and petroleum spirits (40—60 °C). The solid compound was collected and analysed by ^{1}H NMR.

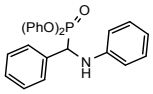
Dimers



A round bottom flask was charged with aldehyde (1.00 mmol), which was dissolved in either $[G3(Li)]^+$ TFSI or $[G4(Li)]^+$ TFSI (0.5 mL). Phenylenediamine (0.5 mmol) was then added, before the addition of diphenyl phosphite (0.299 mL, 1.56 mmol) and stirred at room temperature for 10 minutes. Diethyl ether (10 mL) was added at the conclusion of the reaction, before the addition of deionised water (10 mL). Precipitate formed from the organic phase at reduced temperature (0 °C – r.t.), which was then filtered washing with excess water and petroleum spirits (40—60 °C). This process may have been repeated to obtain any product that may have remained in the organic phase after filtration. Any purification was achieved through redissolving crude material in Et_2O and repeating the above process. The solid compound was collected and analysed by ^{1}H NMR.

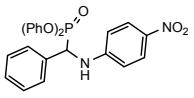
Compound reports

Diphenyl (phenyl(phenylamino)methyl)phosphonate 3



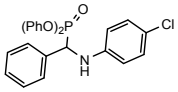
White solid (0.377 g, 91%). Analytically pure by ^{1}H NMR and consistent with literature reports[1]. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.55 (2H, m, Ar-H), 7.22 (14H, m, Ar-H), 6.85 (2H, m, Ar-H), 6.74 (1H, m, Ar-H), 6.65 (2H, m, Ar-H), 5.14 (1H, d, $J_{H\text{-}P}$ = 27 Hz, C*H*), N*H* not seen.

Diphenyl (((4-nitrophenyl)amino)(phenyl)methyl)phosphonate 5a



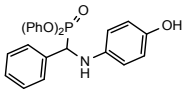
Sandy-brown solid (0.297 g, 64%). Analytically pure by ^{1}H NMR and consistent with literature reports[1]. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.97 (2H, d, *J* = 8.1 Hz, Ar-H), 7.52 (2H, m, Ar-H), 7.22 (12H, m, Ar-H), 6.72 (2H, d, *J* = 8.1 Hz Ar-H), 6.57 (2H, d, *J* = 8.1 Hz, Ar-*H*), 6.14 (1H, bs, N*H*) 5.18 (1H, dd, $J_{H\text{-}P}$ = 8.1, 24.3 Hz, C*H*).

Diphenyl (((4-chlorophenyl)amino)(phenyl)methyl)phosphonate 5b



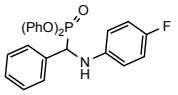
White solid (0.430 g, 96%). Analytically pure by ^{1}H NMR and consistent with literature reports[1]. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.52 (2H, m, Ar-H), 7.17 (12H, m, Ar-H), 6.82 (2H, m, Ar-H), 6.56 (2H, m, Ar-H), 5.07 (1H, d, $J_{H\text{-}P}$ = 27 Hz, C*H*), N*H* not seen.

Diphenyl (((4-hydroxyphenyl)amino)(phenyl)methyl)phosphonate 5c



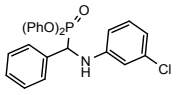
White solid (0.395 g, 92%); **m.p.** 118.2 °C; **^{1}H NMR** (270 MHz, $CDCl_3$): δ 7.53 (2H, m, Ar-*H*), 7.36-7.07 (11H, m, Ar-*H*), 6.84 (2H, m, Ar-*H*), 6.63 (2H, d, *J* = 8 Hz, Ar-*H*), 6.54 (2H, d, *J* = 8 Hz, Ar-*H*), 5.04 (1H, d, $J_{H\text{-}P}$ = 24 Hz, C*H*), N*H* and O*H* not seen; **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.39, 150.32, 150.23, 148.81, 129.82, 129.72, 128.91, 128.89, 128.44, 128.34, 128.28, 125.48/ 125.30/ 120.80/ 120.76/ 120.45/ 120.40/ 116.23/ 115.82/ 71.89/ 70.45/ 59.13; **^{31}P NMR** (202 MHz, $CDCl_3$): δ 16.10; **HRMS (ESI)** calculated for $[C_{25}H_{22}NO_4P + H]^+$: 432.1359, found 432.1361.

Diphenyl (((4-fluorophenyl)amino)(phenyl)methyl)phosphonate 5d



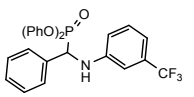
White solid (0.364 g, 84%). Analytically pure by ^{1}H NMR and consistent with literature reports[1]. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.52 (2H, m, Ar-H), 7.23 (13H, m, Ar-H), 6.83 (4H, m, Ar-H), 6.58 (2H, m, Ar-H), 5.06 (1H, d, $J_{H\text{-}P}$ = 24.3 Hz, C*H*), N*H* not seen.

Diphenyl (((3-chlorophenyl)amino)(phenyl)methyl)phosphonate 5e



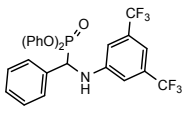
White solid (0.393 g, 81%); **m.p.** 135.5 °C; **^{1}H NMR** (270 MHz, $CDCl_3$): δ 7.54 (2H, m, Ar-*H*), 7.34 (8H, m, Ar-*H*), 7.20 (2H, m, Ar-*H*), 7.07 (3H, m, Ar-*H*), 6.82 (2H, m, Ar-*H*), 6.70 (1H, m, Ar-*H*), 6.63 (1H, m, Ar-*H*), 6.50 (1H, m, Ar-*H*) 5.09 (1H, d, $J_{H\text{-}P}$ = 16.2 Hz, C*H*), N*H* not seen; **^{13}C NMR** (100 MHz, $CDCl_3$): δ 130.38, 129.90, 129.76, 129.05, 128.23, 125.61, 123.97, 120.70, 120.66, 120.35, 120.31, 113.92, 112.28; **^{31}P NMR** (160 MHz, $CDCl_3$): δ 15.33; **HRMS (ESI)** calculated for $[C_{25}H_{21}ClNO_3P + H]^+$: 450.1020, found 450.1014.

Diphenyl (phenyl((3-(trifluoromethyl)phenyl)amino)methyl) phosphonate 5f



Off-white solid (0.414 g, 86%); **m.p.** 122.1 °C; **^{1}H NMR** (270 MHz, $CDCl_3$): δ 7.54 (2H, m, Ar-*H*), 7.40-7.06 (12H, m, Ar-*H*), 6.98 (1H, m, Ar-*H*), 6.80 (4H, m, Ar-*H*), 5.14 (1H, d, $J_{H\text{-}P}$ = 24.3 Hz, C*H*), N*H* not seen; **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.35, 146.09, 134.21, 129.91, 129.86, 129.76, 129.10, 129.07, 128.77, 128.74, 128.24, 128.18, 125.64, 125.44, 120.67, 120.63, 120.33, 120.29, 116.84, 110.54, 56.70, 55.16; **^{31}P NMR** (160 MHz, $CDCl_3$): δ 15.23; **HRMS (ESI)** calculated for $[C_{26}H_{21}F_3NO_3P + H]^+$: 484.1284, found 484.1331.

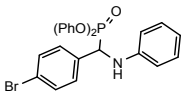
Diphenyl (phenyl((3,5-bis(trifluoromethyl)phenyl)amino)methyl) phosphonate 5g



White solid (0.331 g, 60%); **m.p.** 138.4 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.54 (2H, m, Ar-*H*), 7.41-7.34 (3H, m, Ar-*H*), 7.31-7.27 (3H, m, Ar-*H*), 7.22-7.16 (4H, m, Ar-*H*), 7.13-7.08 (3H, m, Ar-*H*), 6.98 (2H, s, Ar-*H*), 6.78 (2H, m, Ar-*H*), 5.41 (1H, bs, N*H*), 5.15 (1H, d, $J_{H\text{-}P}$ = 24 Hz, C*H*); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 129.98, 129.78, 129.28, 129.26, 129.05, 128.20, 128.14, 125.78, 125.53, 120.56,

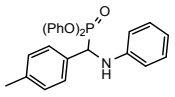
120.52, 120.21, 120.17, 97.26; **^{31}P NMR** (160 MHz, $CDCl_3$): δ 14.54; **HRMS (ESI)** calculated for $[C_{27}H_{20}F_6NO_3P + H]^+$: 552.1158, found 552.1225.

Diphenyl ((4-bromophenyl)(phenylamino)methyl)phosphonate 7a



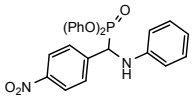
White solid (0.451 g, 91%). Analytically pure by ^{1}H NMR and consistent with literature reports[1]. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.46 (4H, m, Ar-H), 7.32-7.06 (10H, m, Ar-H), 6.92 (2H, m, Ar-H), 6.77 (1H, m, Ar-H), 6.60 (2H, m, Ar-H), 5.09 (1H, d, $J_{H\text{-}P}$ = 24.3 Hz, C*H*), N*H* not seen.

Diphenyl ((phenylamino)(p-tolyl)methyl)phosphonate 7b



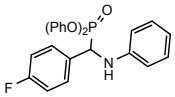
White solid (0.384 g, 90%). Analytically pure by ^{1}H NMR and consistent with literature reports[1]. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.44 (2H, m, Ar-H), 7.31-7.07 (12H, m, Ar-H), 6.88 (2H, m, Ar-H), 6.74 (1H, m, Ar-H), 6.65 (2H, m, Ar-H), 5.12 (1H, d, $J_{H\text{-}P}$ = 24.3 Hz, C*H*), 2.33 (3H, s, CH_3), N*H* not seen.

Diphenyl ((4-nitrophenyl)(phenylamino)methyl)phosphonate 7c



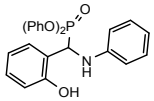
Sandy-yellow solid (0.320 g, 69%). Analytically pure by ^{1}H NMR and consistent with literature reports[1]. ^{1}H NMR (270 MHz, $CDCl_3$): δ 8.21 (2H, m, Ar-H), 7.75 (2H, m, Ar-H), 7.32-7.06 (10H, m, Ar-H), 6.95 (2H, m, Ar-H), 6.79 (1H, m, Ar-H), 6.58 (2H, m, Ar-H), 5.23 (1H, d, $J_{H\text{-}P}$ = 24.3 Hz, C*H*), N*H* not seen.

Diphenyl ((4-fluorophenyl)(phenylamino)methyl)phosphonate 7d



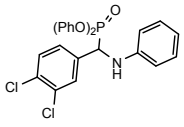
White solid (0.337 g, 78%). Analytically pure by ^{1}H NMR and consistent with literature reports[1]. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.52 (2H, m, Ar-H), 7.32-7.00 (12H, m, Ar-H), 6.90 (2H, m, Ar-H), 6.76 (1H, m, Ar-H), 6.63 (2H, m, Ar-H), 5.12 (1H, d, $J_{H\text{-}P}$ = 24.3 Hz, C*H*), N*H* not seen.

Diphenyl ((2-hydroxyphenyl)(phenylamino)methyl)phosphonate 7e



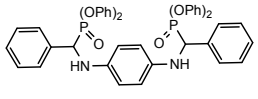
White solid (0.360 g, 84%). Analytically pure by ^{1}H NMR and consistent with literature reports[2]. **^{1}H NMR** (270 MHz, $CDCl_3$): δ 7.32-7.23 (5H, m, Ar-*H*), 7.19-7.13 (5H, m, Ar-*H*), 7.04 (2H, d, *J* = 8 Hz, Ar-*H*), 6.98 (2H, d, *J* = 8 Hz, Ar-*H*), 6.90-6.79 (3H, m, Ar-*H*), 6.75 (2H, d, *J* = 8 Hz, Ar-*H*), 5.35 (1H, d, $J_{H\text{-}P}$ = 24 Hz, C*H*), N*H* not seen

Diphenyl ((3,4-dichlorophenyl)(phenylamino)methyl)phosphonate 7f



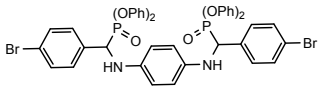
White solid (0.382 g, 79%); **m.p.** 162.7 °C; **^{1}H NMR** (500 MHz, DMSO-d_6): δ 8.00 (1H, s, Ar-*H*), 7.71 (1H, m, Ar-*H*), 7.66 (1H, d, *J* = 8.4 Hz, Ar-*H*), 7.35 (4H, m, Ar-*H*), 7.19 (2H, m, Ar-*H*), 7.09 (4H, m, Ar-*H*), 6.98 (2H, d, *J* = 8.7 Hz, Ar-*H*), 6.92 (2H, d, *J* = 7.7 Hz, Ar-*H*), 6.86 (1H, dd, *J* = 5.3, 10.9 Hz, N*H*), 6.62 (1H, app. t, Ar-*H*), 5.77 (1H, dd, *J* = 10.9 Hz, $J_{H\text{-}P}$ = 26.4 Hz, C*H*); **^{13}C NMR** (126 MHz, DMSO-d_6) δ 150.55, 150.47, 150.30, 150.22, 147.05, 146.93, 137.69, 131.48, 131.45, 131.11, 131.08, 131.01, 130.96, 130.93, 130.37, 130.28, 129.47, 129.42, 129.35, 125.81, 121.01, 120.98, 120.71, 120.68, 118.17, 114.25, 54.27, 53.02; **^{31}P NMR** (202 MHz, DMSO-d_6): δ 15.42; **HRMS (ESI)** calculated for $[C_{25}H_{20}Cl_2NO_3P + H]^+$: 484.0631, found 484.0687.

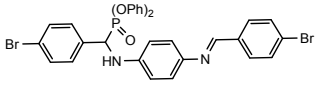
Tetraphenyl ((1,4-phenylenebis(azanediyl))bis(phenylmethylene)) bis(phosphonate) 9a



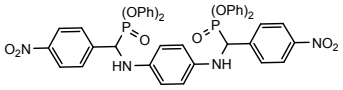
Chalky, white solid (0.242 g, 64%); **m.p.** 184.0 °C; **^{1}H NMR** (500 MHz, DMSO-d_6): δ 7.67 (4H, m, Ar-*H*), 7.38-7.30 (14H, m, Ar-*H*), 7.19 (4H, m, Ar-*H*), 7.10 (4H, m, Ar-*H*), 6.86 (4H, m, Ar-*H*), 6.72 (4H, d, Ar-*H*), 6.13 (2H, m, N*H*), 5.43 (2H, dd, $J_{H\text{-}P}$ = 10, 25 Hz, C*H*); **^{13}C NMR** (126 MHz, DMSO-d_6): δ 150.71, 150.63, 150.45, 150.37, 139.38, 139.30, 139.25, 139.17, 136.46, 130.19, 130.17, 129.83, 129.19, 129.14, 128.64, 128.24, 125.59, 125.54, 121.14, 121.11, 120.79, 120.76, 115.67, 115.57, 115.55, 56.46, 56.41, 55.21, 55.16; **^{31}P NMR** (202 MHz, DMSO-d_6): δ 17.11 (d, $J_{P\text{-}P}$ = 24.24); **HRMS (ESI)** calculated for $[C_{44}H_{38}N_2O_6P_2 + H]^+$: 753.2278, found 753.2360.

Tetraphenyl ((1,4-phenylenebis(azanediyl))bis((4-bromophenyl)methylene))bis(phosphonate) 9b



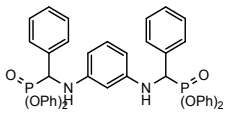
Chalky, white solid (0.295 g, 65%); **m.p.** 206.5 °C; **^{1}H NMR** (500 MHz, DMSO-d_6): δ 7.59 (4H, m, Ar-*H*), 7.53 (4H, m, Ar-*H*), 7.31 (8H, m, Ar-*H*), 7.16 (4H, m, Ar-*H*), 7.06 (4H, m, Ar-*H*), 6.93 (4H, m, Ar-*H*), 6.67 (4H, m, Ar-*H*), 6.15 (2H, m, 2N*H*), 5.44 (2H, dd, $J_{H\text{-}P}$ = 10.9, 26.15 Hz, 2C*H*); **^{13}C NMR** (126 MHz, DMSO-d_6): δ 150.65,  150.57, 150.37, 150.29, 139.15, 139.02, 136.13, 131.57, 131.31, 131.26, 130.27, 130.20, 125.65, 121.58, 121.54, 121.09, 121.06, 120.77, 120.74, 115.59, 55.77, 54.52.; **^{31}P NMR** (202 MHz, DMSO-d_6): δ 16.32; **HRMS (ESI)** calculated for $[C_{44}H_{36}Br_2N_2O_6P_2 + H]^+$: 911.0468, found 911.0689, fragment $[C_{32}H_{25}Br_2N_2O_6P_2 + H]^+$: 677.0022, found 677.0105.

Tetraphenyl ((1,4-phenylenebis(azanediyl))bis((4-nitrophenyl)methylene))bis(phosphonate) 9c



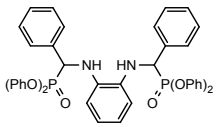
Mustard-yellow solid (0.141 g, 33%); **m.p.** 141.8 °C; **^{1}H NMR** (500 MHz, DMSO-d_6): δ 8.27 (4H, d, *J* = 8.1 Hz, Ar-*H*), 7.86 (4H, m, Ar-*H*), 7.36 (8H, m, Ar-*H*), 7.19 (7H, m, Ar-*H*), 7.09 (8H, m, Ar-*H*), 6.75 (1H, m, Ar-*H*), 5.71 (2H, m, 2C*H*), 2N*H* not seen; **^{13}C NMR** (126 MHz, DMSO-d_6): δ 157.76, 150.55, 150.47, 150.43, 150.35, 147.63, 147.60, 145.51, 130.34, 130.29, 129.82, 129.16, 129.11, 125.72, 125.67, 123.69, 123.66, 120.91, 120.88, 120.85, 119.24, 115.66, 69.80, 68.50; **^{31}P NMR** (202 MHz, DMSO-d_6): δ 14.29; **HRMS (ESI)** calculated for $[C_{44}H_{37}N_4O_{10}P_2 + H]^+$: 843.1979, found 843.1978,

Tetraphenyl ((1,3-phenylenebis(azanediyl))bis(phenylmethylene))bis(phosphonate) 11



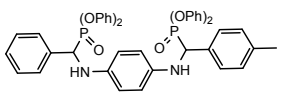
Chalky, white solid (0.128 g, 34%); **m.p.** 95.5 °C; **^{1}H NMR** (500 MHz, DMSO-d_6): δ 7.64 (4H, m, Ar-*H*), 7.30 (15H, m, Ar-*H*), 7.15 (4H, m, Ar-*H*), 7.08 (4H, m, Ar-*H*), 6.84 (4H, m, Ar-*H*), 6.74 (1H, m, Ar-*H*), 6.48 (2H, bs, 2N*H*), 6.23 (2H, m, Ar-*H*), 5.56 (2H, m, 2C*H*); **^{13}C NMR** (126 MHz, DMSO-d_6): δ 157.76, 150.68, 150.60, 150.41, 150.33, 148.25, 148.12, 136.40, 136.33, 130.22, 130.19, 130.16, 129.83, 129.54, 129.21, 129.16, 128.63, 128.26, 128.24, 125.66, 125.61, 121.18, 121.16, 121.13, 121.10, 120.81, 120.78, 119.25, 115.67, 105.20, 98.11, 55.24, 53.99.; **^{31}P NMR** (202 MHz, DMSO-d_6): δ 17.00; **HRMS (ESI)** calculated for $[C_{44}H_{38}N_2O_6P_2 + H]^+$: 753.2278, found 753.2281.

Tetraphenyl ((1,2-phenylenebis(azanediyl))bis(phenylmethylene))bis(phosphonate) 13



Yellow/brown solid (0.040 g, 9% by ^{1}H NMR); **m.p.** 145.8 °C; **^{1}H NMR** (500 MHz, DMSO-d_6): δ 8.53 (2H, s, Ar-*H*), 7.65 (4H, d, *J* = 7.35 Hz, Ar-*H*), 7.35 (4H, m, Ar-*H*), 7.29 (4H, m, Ar-*H*), 7.18 (4H, m, Ar-*H*), 7.08 (4H, d, *J* = 7.75 Hz, Ar-*H*), 6.84 (4H, d, *J* = 7.75 Hz, Ar-*H*), 6.74 (4H, d, *J* = 8.05 Hz, Ar-*H*), 6.50 (4H, m, Ar-*H*), 6.15 (2H, m, 2N*H*), 5.41 (2H, dd, $J_{H\text{-}P}$ = 10.95, 25.8 Hz, 2C*H*); **^{13}C NMR** (126 MHz, DMSO-d_6): δ 150.29, 150.21, 150.01, 149.93, 149.42, 139.39, 139.25, 135.96, 129.76, 129.75, 128.78, 128.74, 128.20, 128.19, 127.83, 125.18, 125.12, 120.71, 120.68, 120.36, 120.32, 115.45, 115.35, 64.95, 56.12, 54.87, 15.20. ; **^{31}P NMR** (202 MHz, DMSO-d_6): δ 17.07; **HRMS (ESI)** calculated for $[C_{44}H_{38}N_2O_6P_2 + Na]^+$: 775.2097, found 775.2436

Diphenyl (((4-(((diphenoxyphosphoryl)(p-tolyl)methyl)amino)phenyl)amino)(phenyl)methyl)phosphonate 14

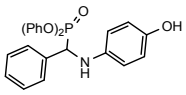


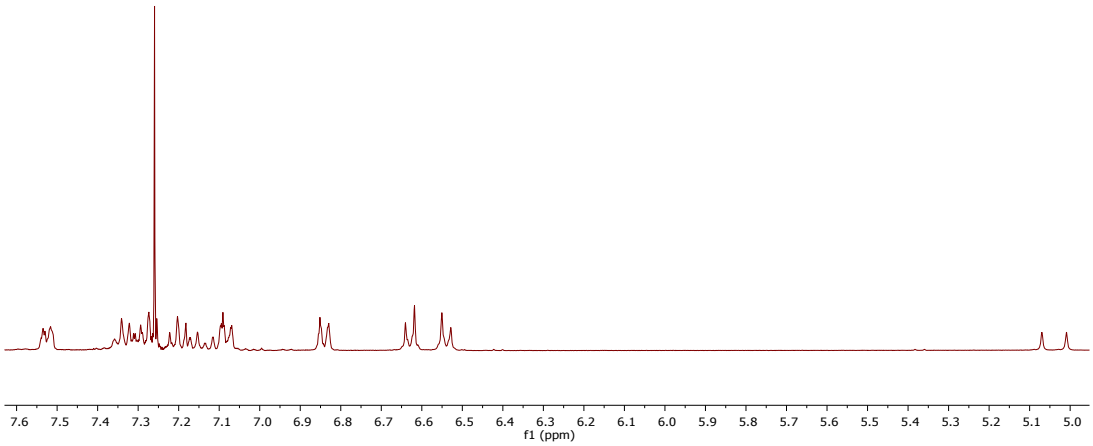
A round bottom flask was charged with benzaldehyde (0.051 mL, 0.5 mmol), which was dissolved in either $[G3(Li)]^+$ TFSI or $[G4(Li)]^+$ TFSI (0.5 mL). 1,4-Phenylenediamine (0.054 g, 0.5 mmol) was then added, before the addition of diphenyl phosphite (0.299 mL, 1.56 mmol) and stirred at room temperature for 5 minutes. Following this, p-tolualdehyde (0.059 mL, 0.5 mmol) was added to the reactionmixture, and allowed to stir for a further 5 mins. Diethyl ether (10 mL) was added at the conclusion of the reaction, before the addition of deionised water (10 mL). Precipitate formed from the organic phase at reduced temperature (0 °C – r.t.), which was then filtered washing with excess water and petroleum spirits (40—60 °C). The solid compound was collected and analysed by ^{1}H NMR, proving to be the desired compound as a chalky, white solid (0.164 g, 43%); **m.p.** 192.2 °C; **^{1}H NMR** (500 MHz, DMSO-d_6): δ 7.63 (2H, m, Ar-*H*), 7.49 (2H, m, Ar-*H*), 7.30 (11H, m, Ar-*H*), 7.13 (6H, m, Ar-*H*), 7.05 (4H, m, Ar-*H*), 6.83 (4H, m, Ar-*H*), 6.66 (4H, q, *J* = 6.2 Hz, Ar-*H*), 6.07 (1H, m, N*H*), 6.01 (1H, m, N*H*), 5.35 (2H, m, 2C*H*), 2.25 (3H, s, CH_3); **^{13}C NMR** (126 MHz, DMSO-d_6): δ 136.47, 133.34, 130.19, 130.16, 129.23,

129.06, 128.64, 125.55, 121.14, 121.11, 120.83, 120.79, 120.76, 115.58, 21.19; **^{31}P NMR** (202 MHz, DMSO-d_6): δ 17.24; **HRMS (ESI)** calculated for $[C_{45}H_{40}N_2O_6P_2 + H]^+$: 767.2434, found 767.2605.

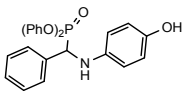
NMR spectra of synthesised compounds.

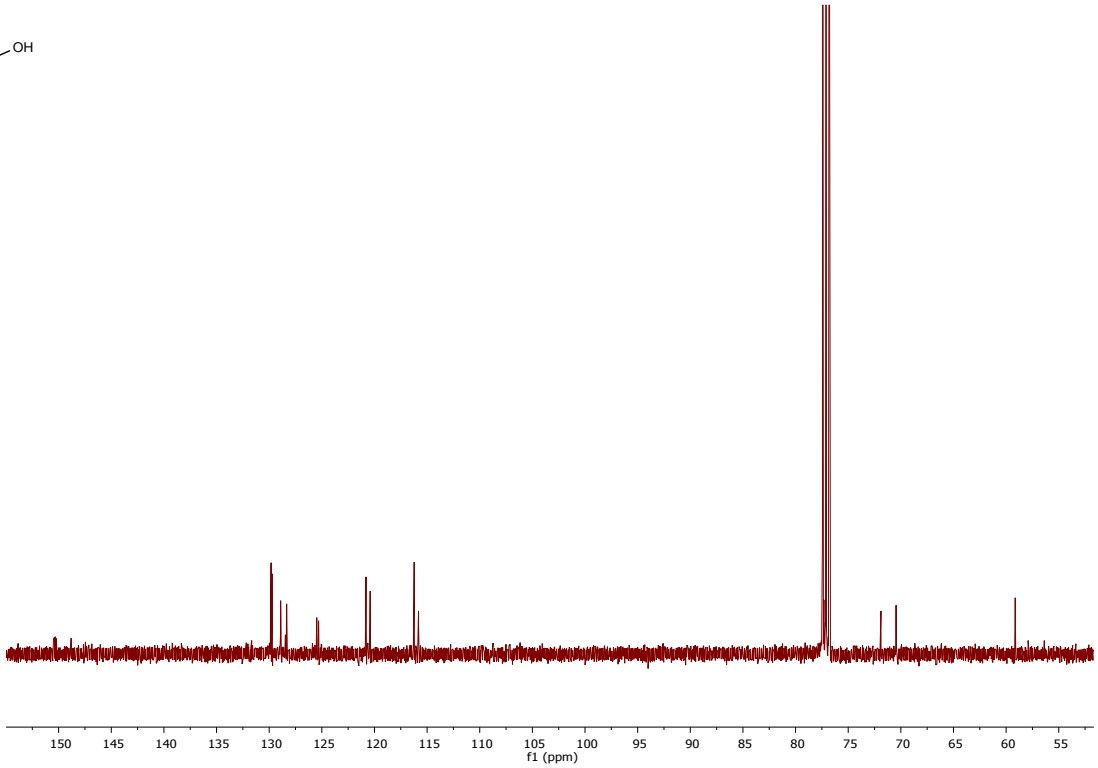
^{1}H NMR (400 MHz, $CDCl_3$) of diphenyl (((4-hydroxyphenyl)amino)(phenyl)methyl)phosphonate **5c**



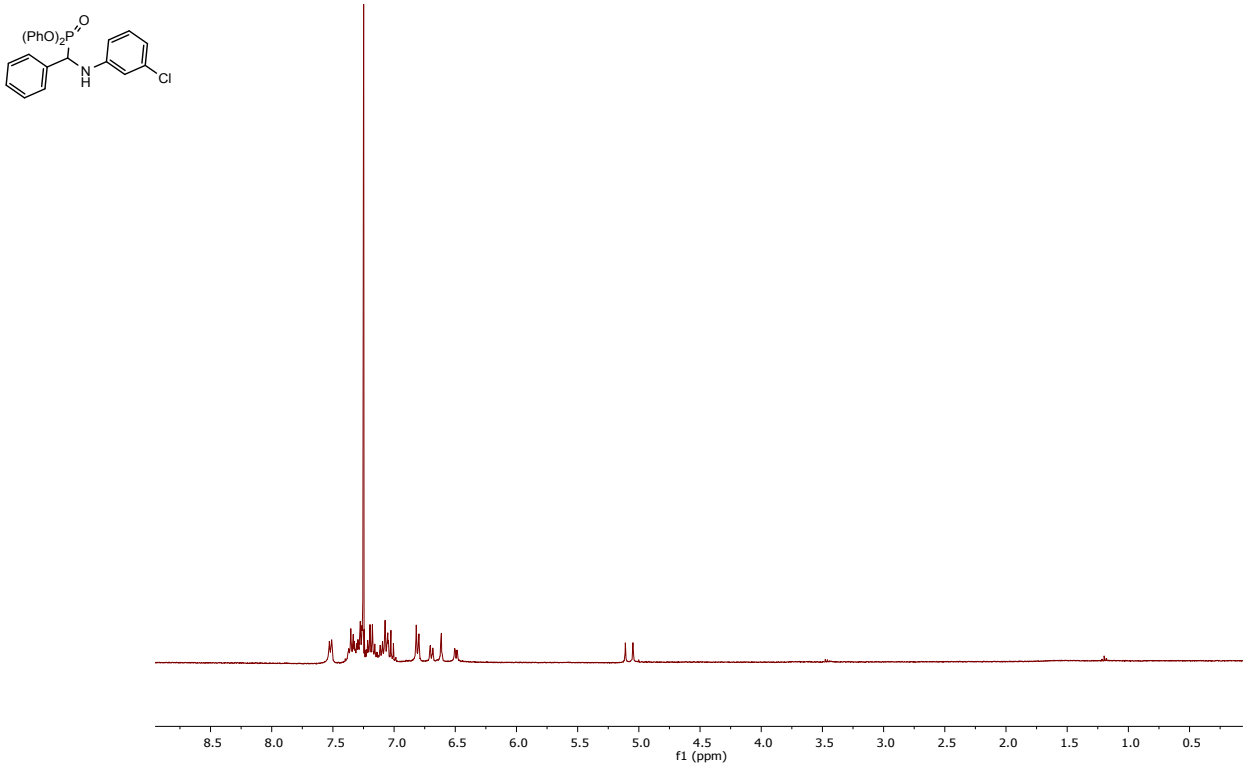


^{13}C NMR (100 MHz, $CDCl_3$) of diphenyl (((4-hydroxyphenyl)amino)(phenyl)methyl)phosphonate **5c**

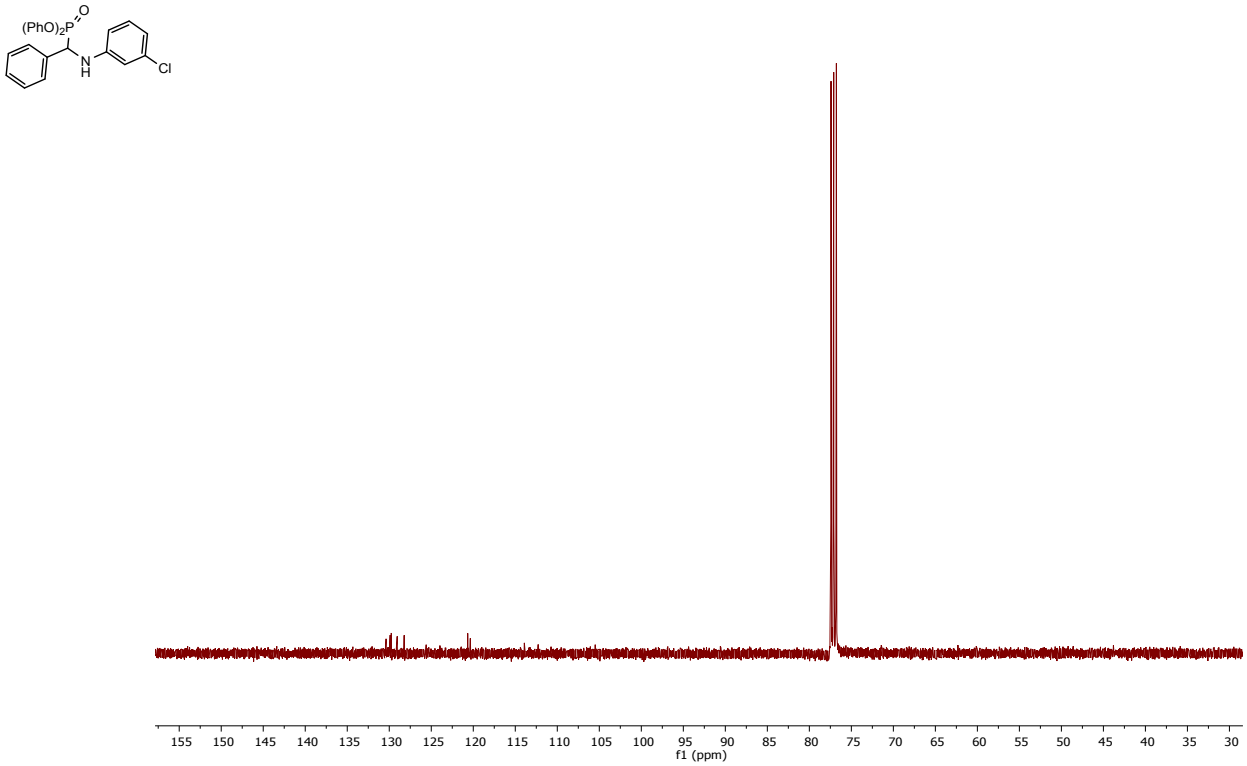




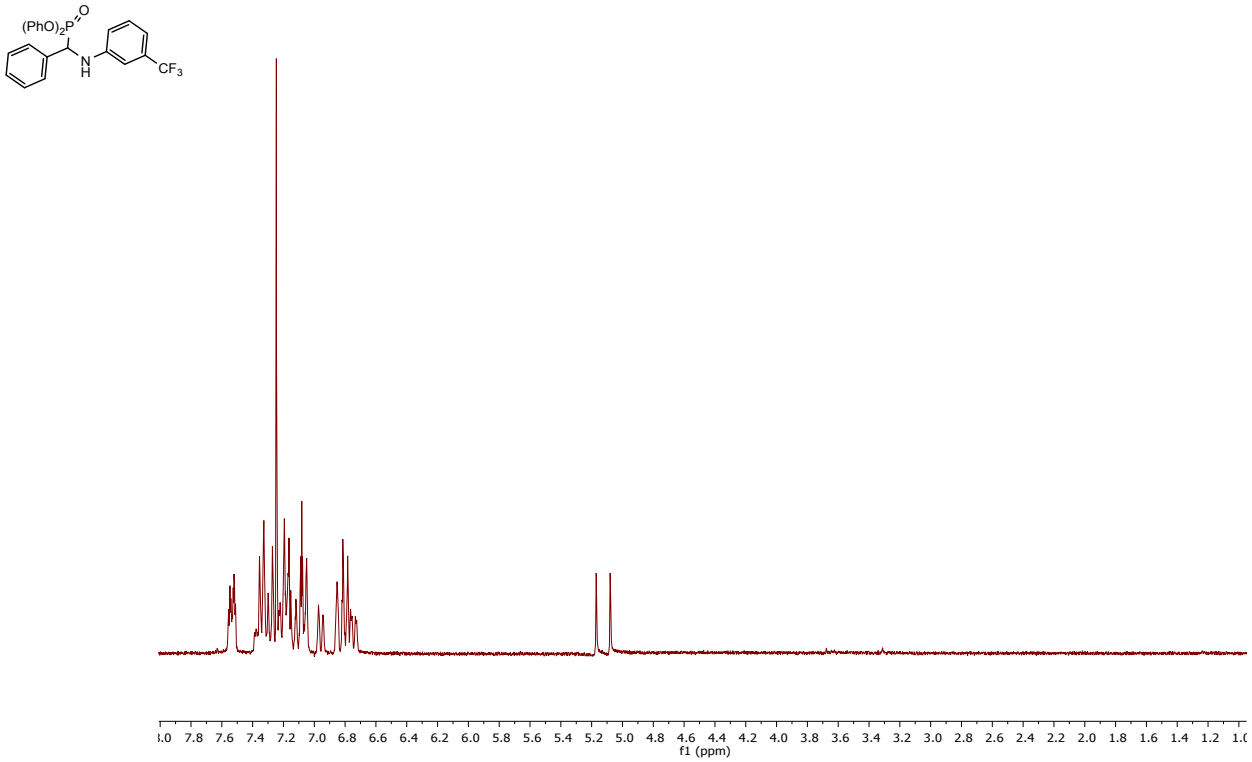
^{1}H NMR (270 MHz, $CDCl_3$) of diphenyl (((3-chlorophenyl)amino)(phenyl)methyl)phosphonate **5e**



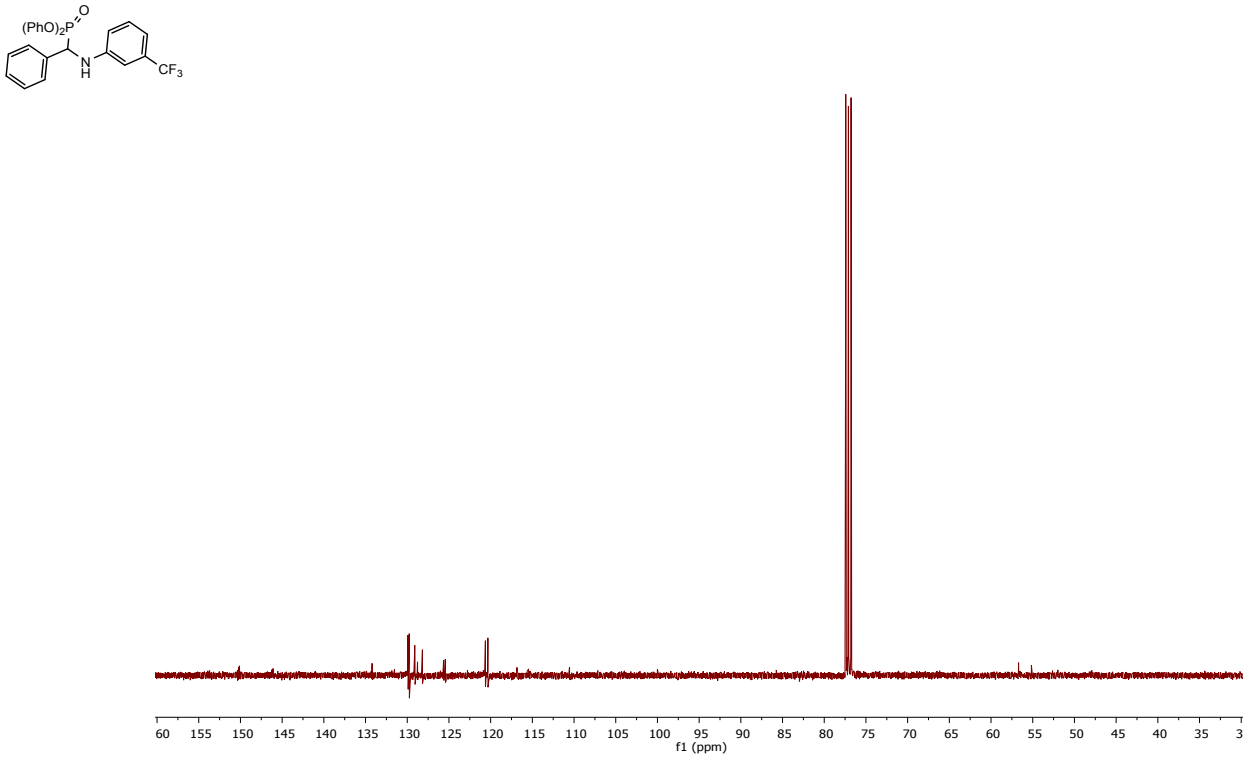
^{13}C NMR (100 MHz, $CDCl_3$) of diphenyl (((3-chlorophenyl)amino)(phenyl)methyl)phosphonate **5e**



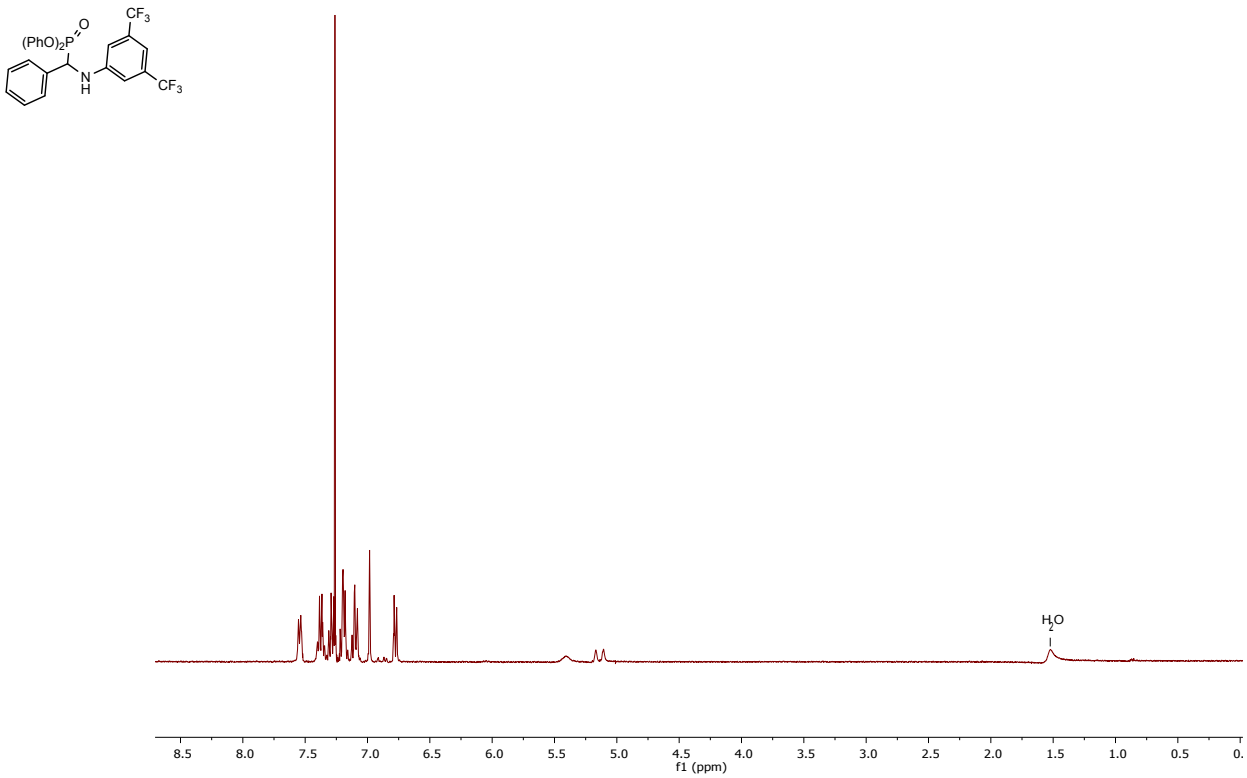
^{1}H NMR (270 MHz, $CDCl_3$) of diphenyl (phenyl((3-(trifluoromethyl)phenyl)amino)methyl) phosphonate **5f**



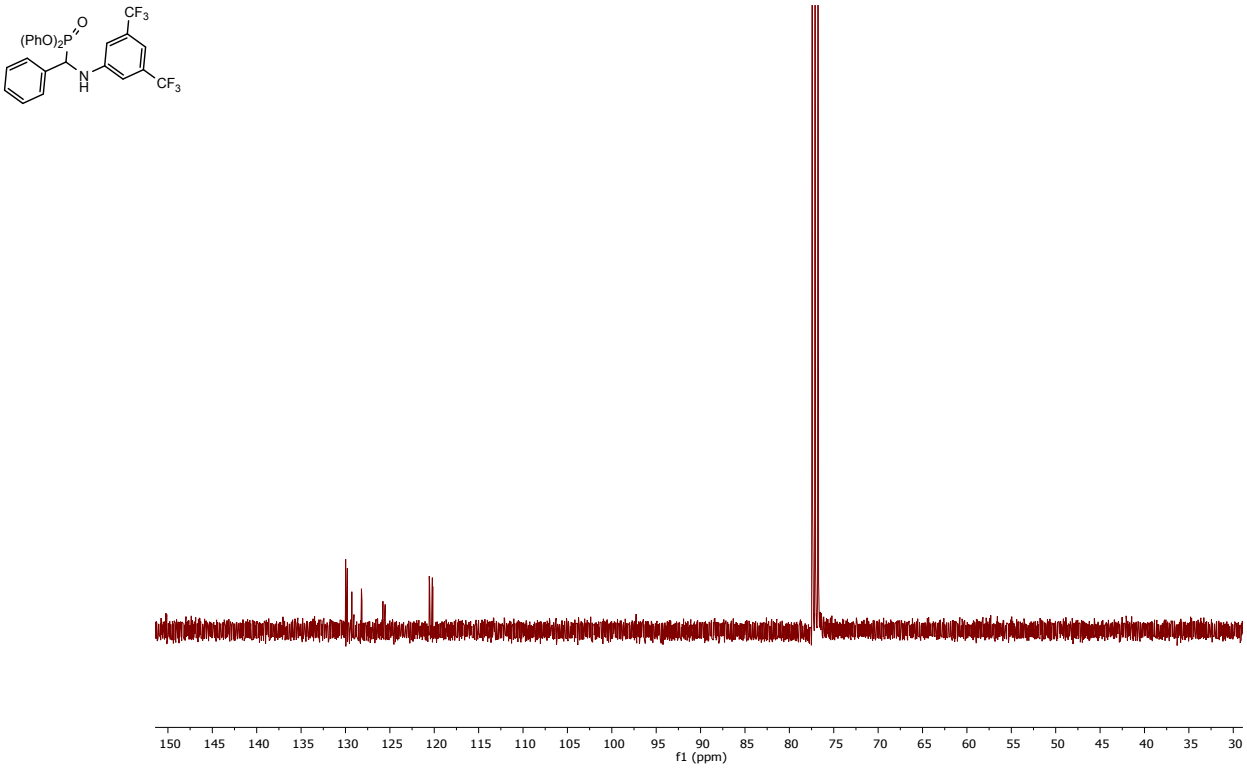
^{13}C NMR (100 MHz, $CDCl_3$) of diphenyl (phenyl((3-(trifluoromethyl)phenyl)amino)methyl) phosphonate **5f**



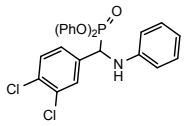
^{1}H NMR (270 MHz, $CDCl_3$) of diphenyl (phenyl((3,5-bis(trifluoromethyl)phenyl)amino)methyl) phosphonate **5g**

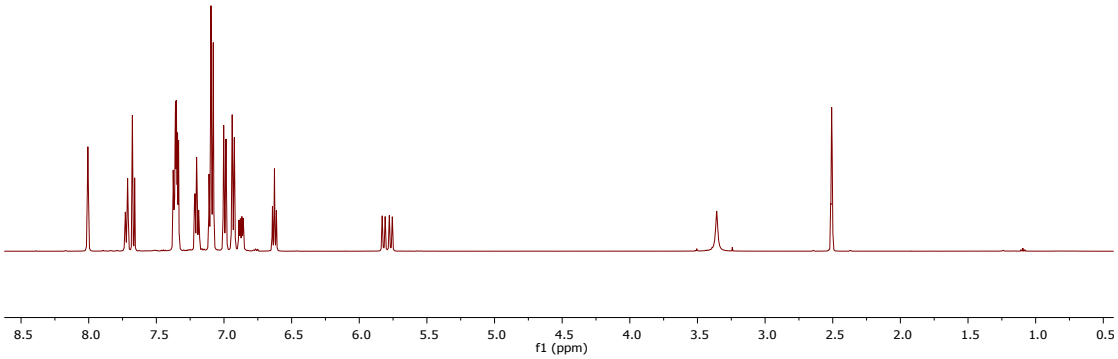


^{13}C NMR (100 MHz, $CDCl_3$) of diphenyl (phenyl((3,5-bis(trifluoromethyl)phenyl)amino)methyl) phosphonate **5g**

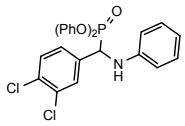


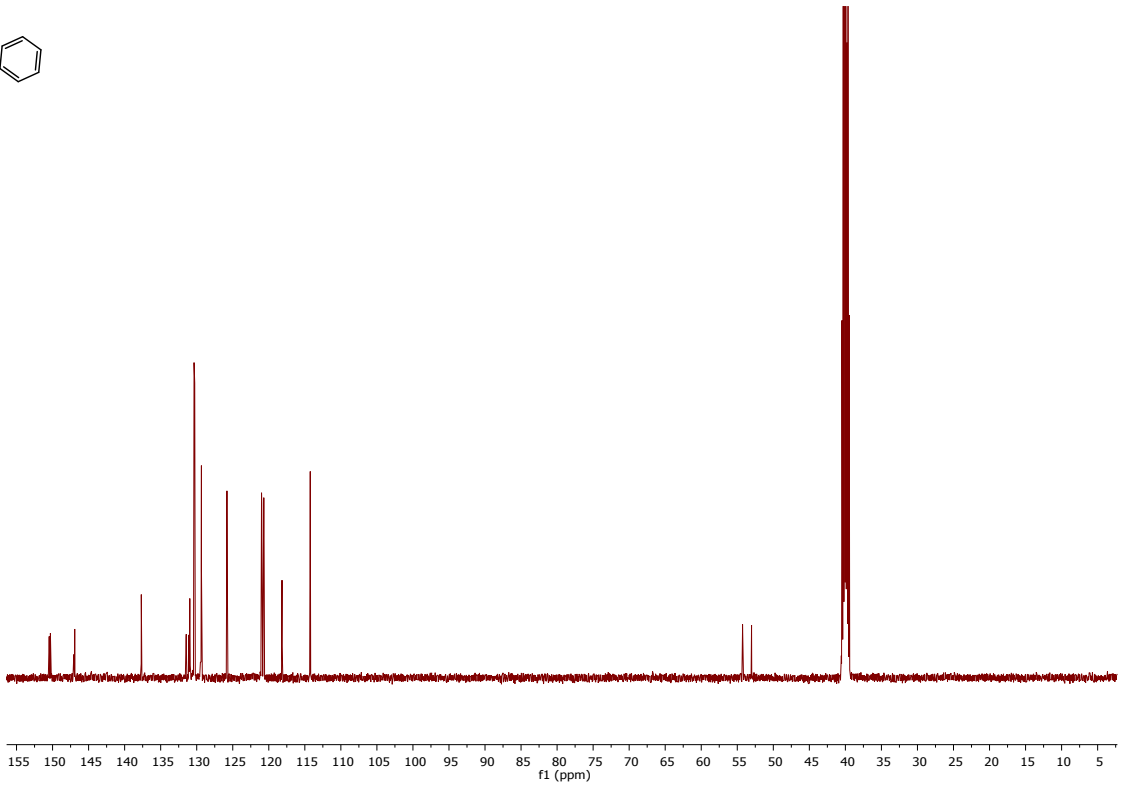
^{1}H NMR (400 MHz, $CDCl_3$) of diphenyl ((3,4-dichlorophenyl)(phenylamino)methyl)phosphonate **7f**



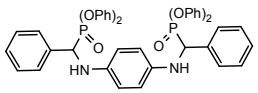


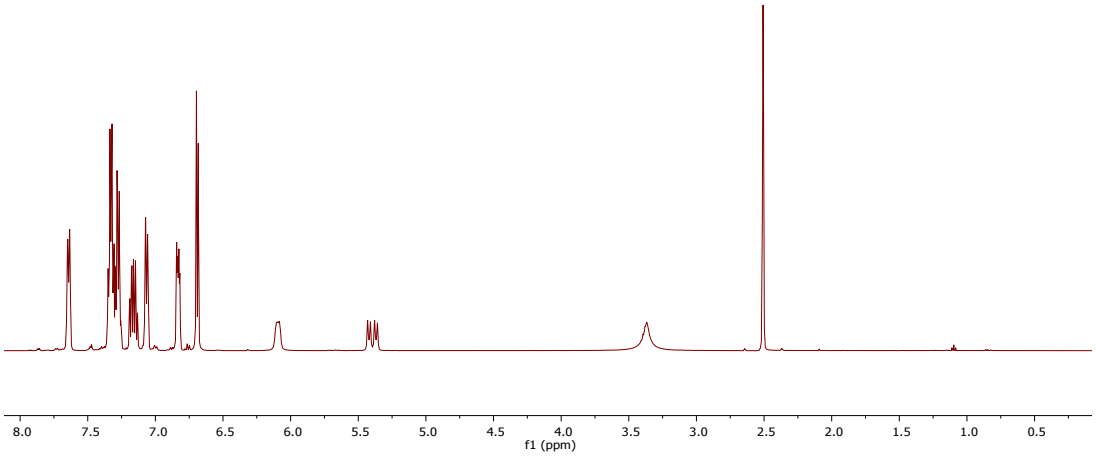
^{13}C NMR (100 MHz, d_6-DMSO) of diphenyl ((3,4-dichlorophenyl)(phenylamino)methyl)phosphonate **7f**



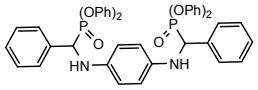


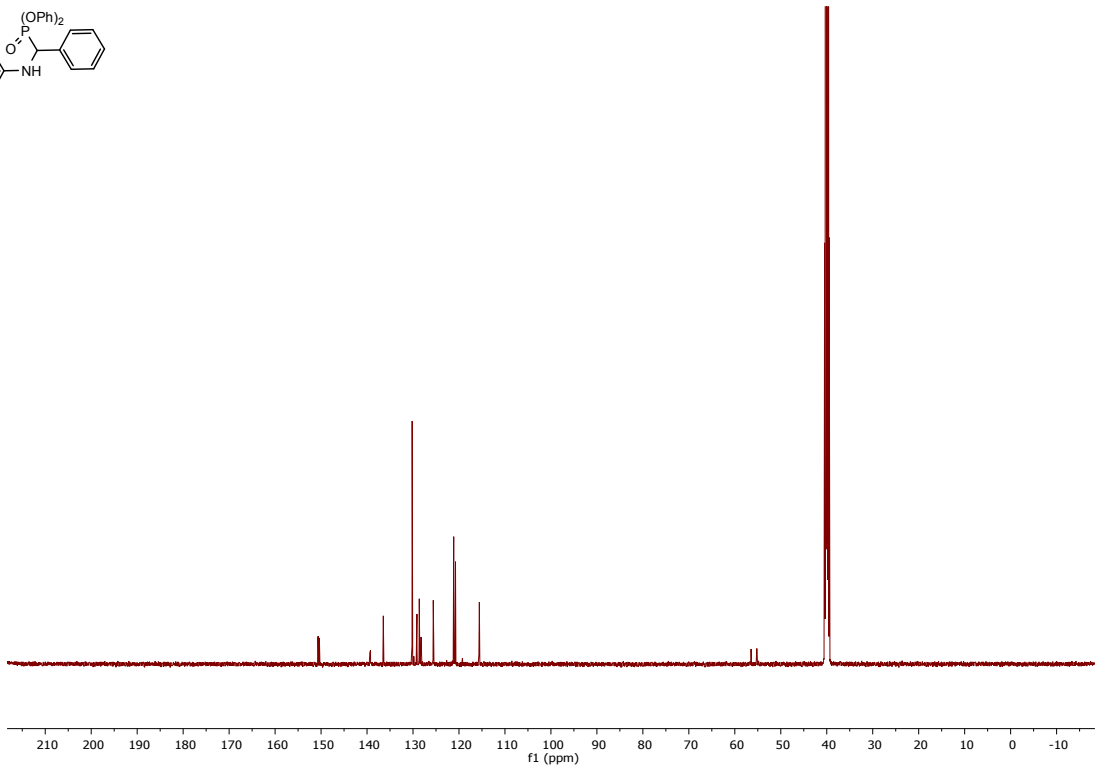
^{1}H NMR (500 MHz, d_6-DMSO) of tetraphenyl ((1,4-phenylenebis(azanediyl))bis(phenylmethylene)) bis(phosphonate) **9a**



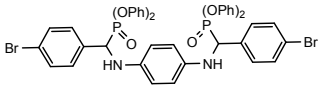


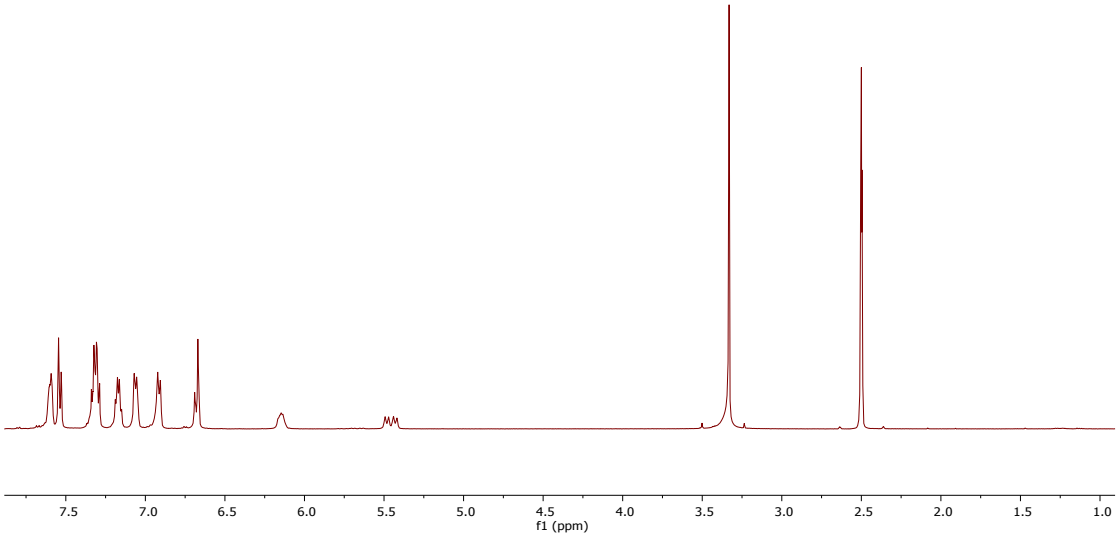
^{13}C NMR (126 MHz, $CDCl_3$) of tetraphenyl ((1,4-phenylenebis(azanediyl))bis(phenylmethylene)) bis(phosphonate) **9a**



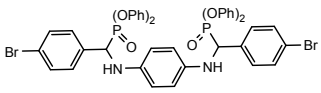


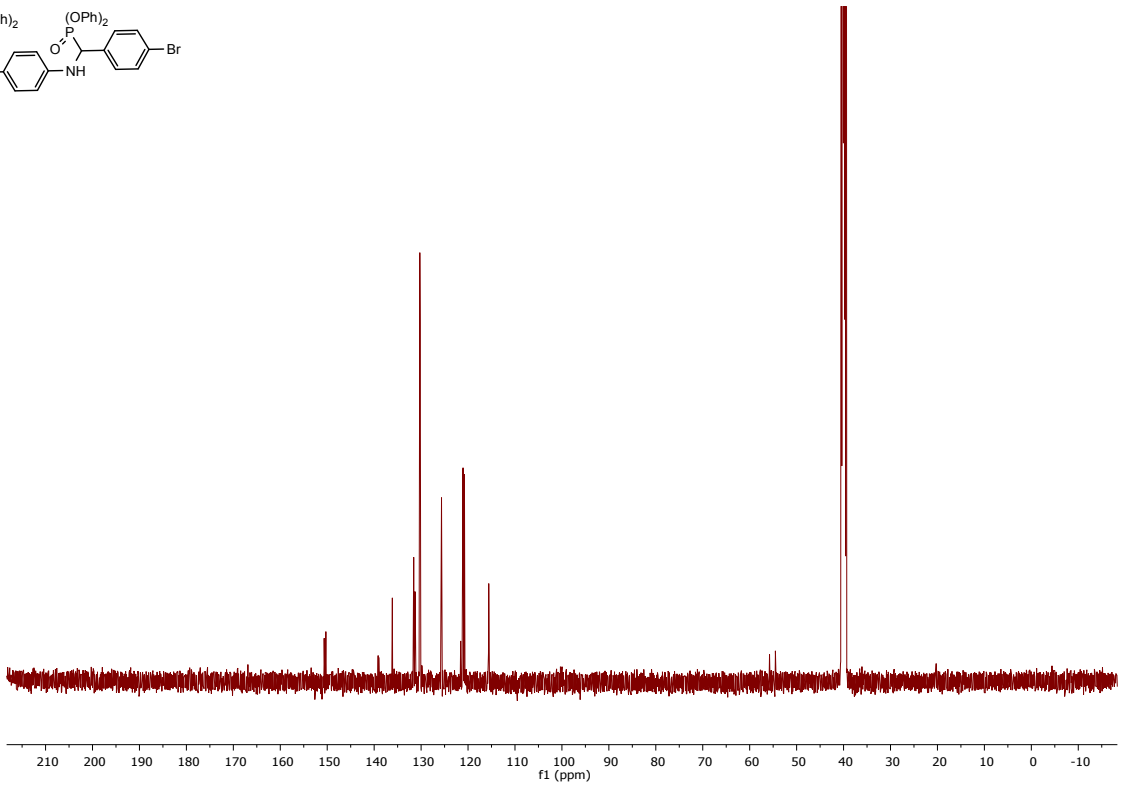
^{1}H NMR (500 MHz, DMSO-d_6) of tetraphenyl ((1,4-phenylenebis(azanediyl))bis((4-bromophenyl)methylene))bis(phosphonate) **9b**



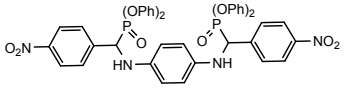


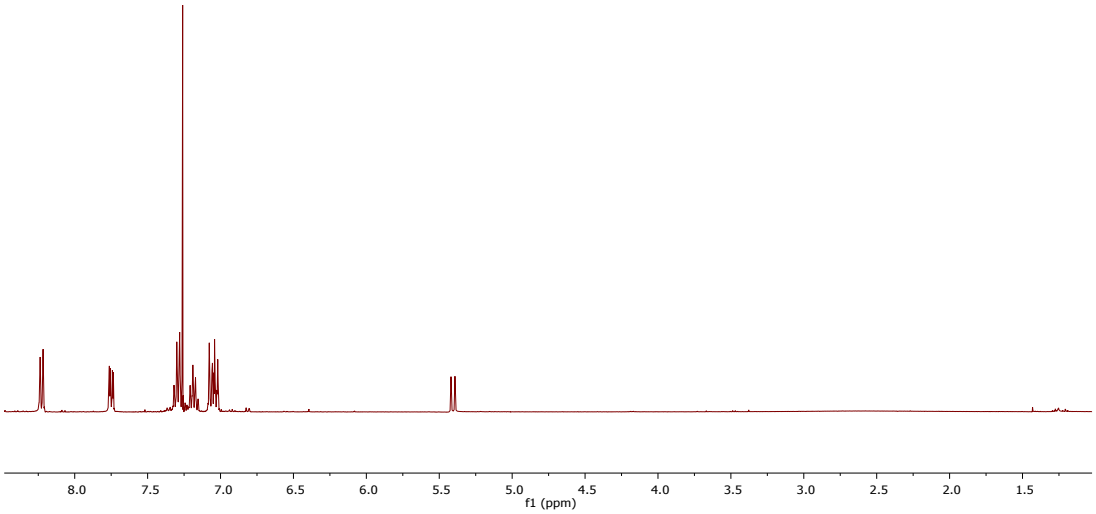
^{13}C NMR (126 MHz, DMSO-d_6) of tetraphenyl ((1,4-phenylenebis(azanediyl))bis((4-bromophenyl)methylene))bis(phosphonate) **9b**



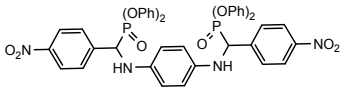


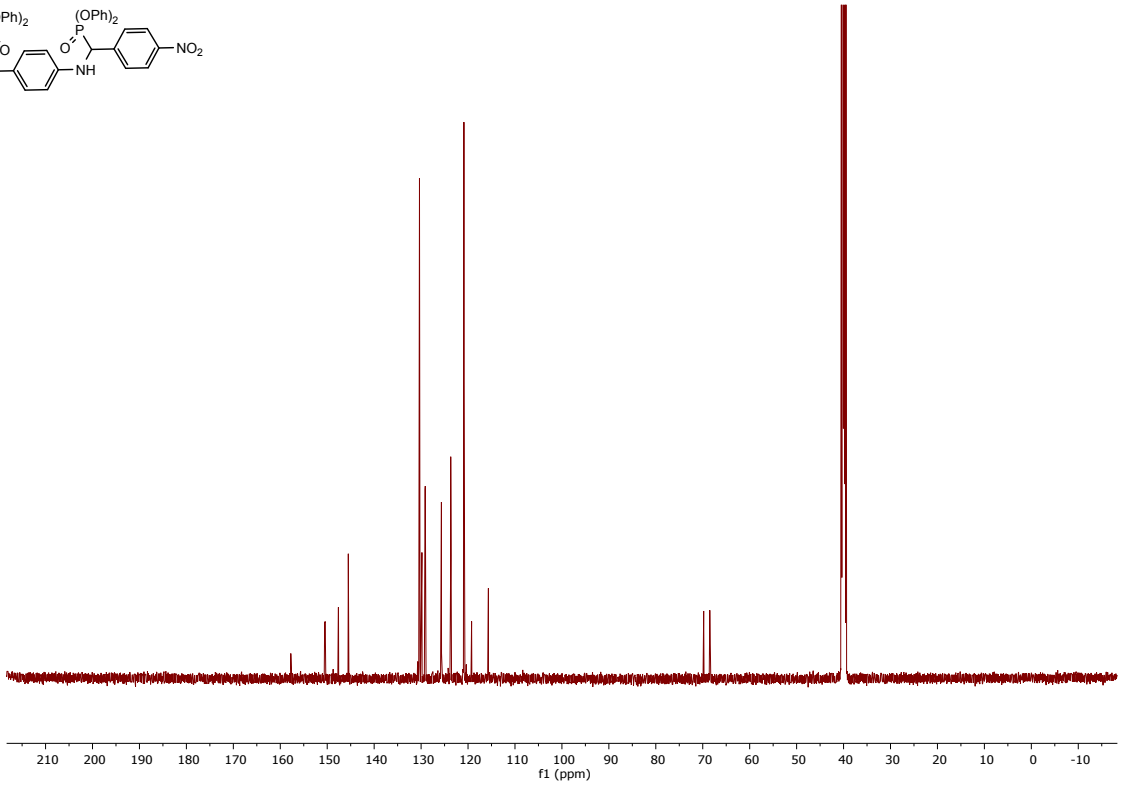
^{1}H NMR (500 MHz, DMSO-d_6) of tetraphenyl ((1,4-phenylenebis(azanediyl))bis((4-nitrophenyl)methylene))bis(phosphonate) **9c**



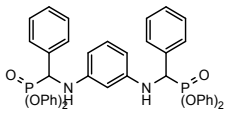


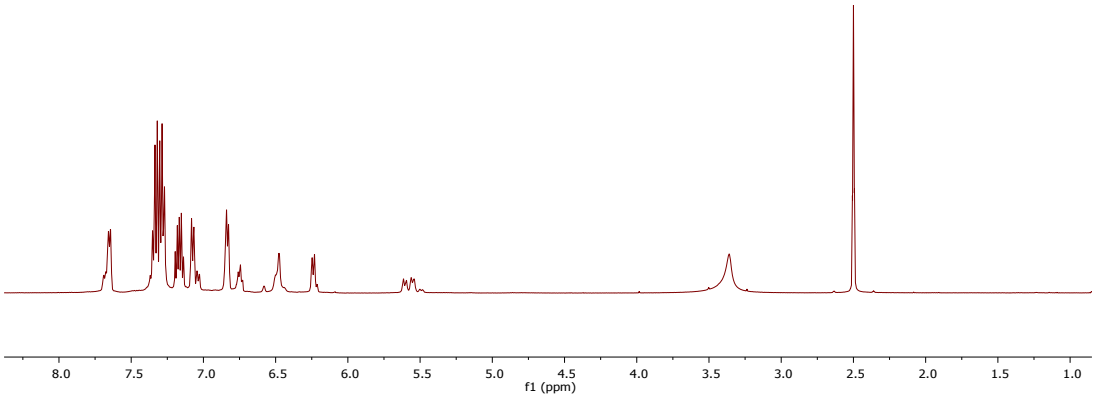
^{13}C NMR (126 MHz, DMSO-d_6) of tetraphenyl ((1,4-phenylenebis(azanediyl))bis((4-nitrophenyl)methylene))bis(phosphonate) **9c**



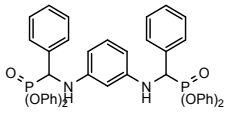


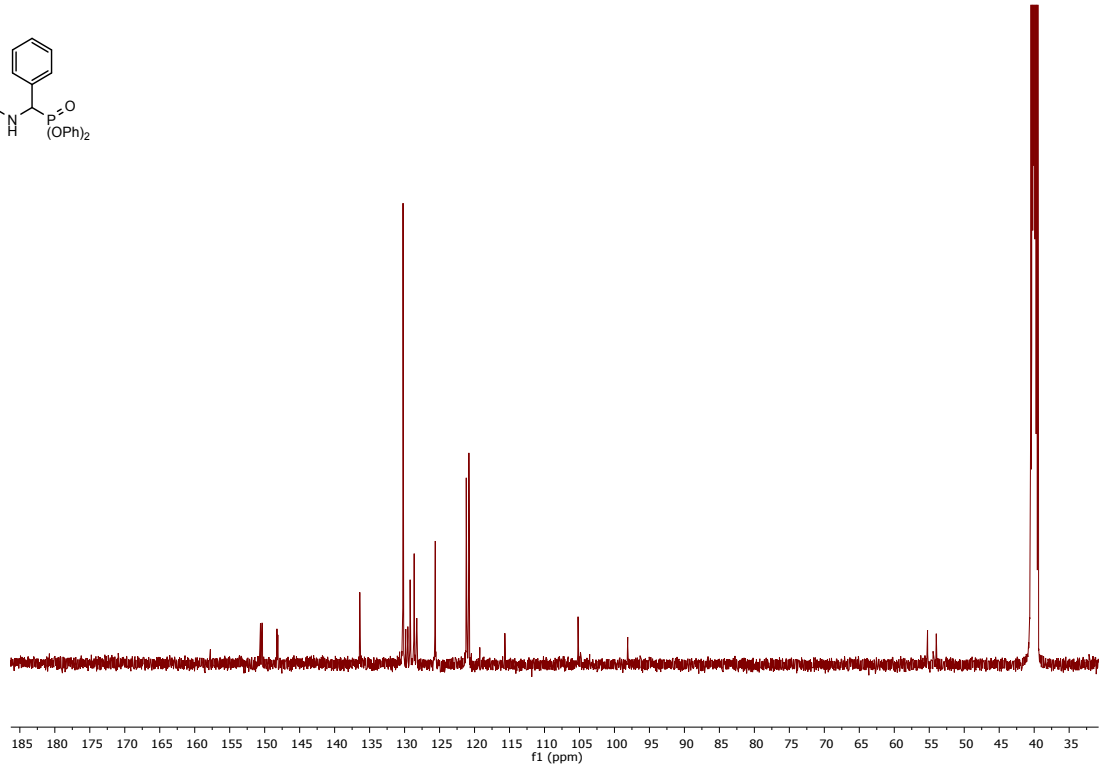
^{1}H NMR (500 MHz, DMSO-d_6) of tetraphenyl ((1,3-phenylenebis(azanediyl))bis(phenylmethylene))bis(phosphonate) **11**



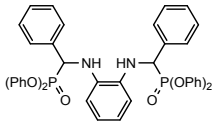


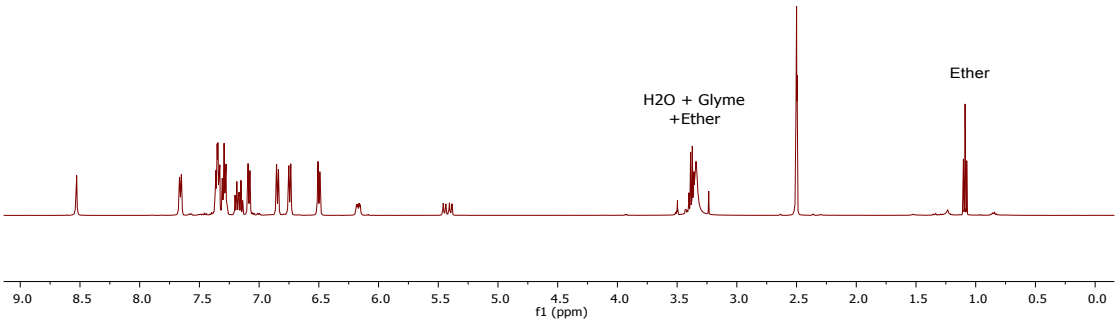
^{13}C NMR (126 MHz, DMSO-d_6) of tetraphenyl ((1,3-phenylenebis(azanediyl))bis(phenylmethylene))bis(phosphonate) **11**



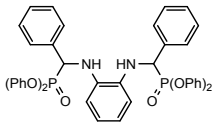


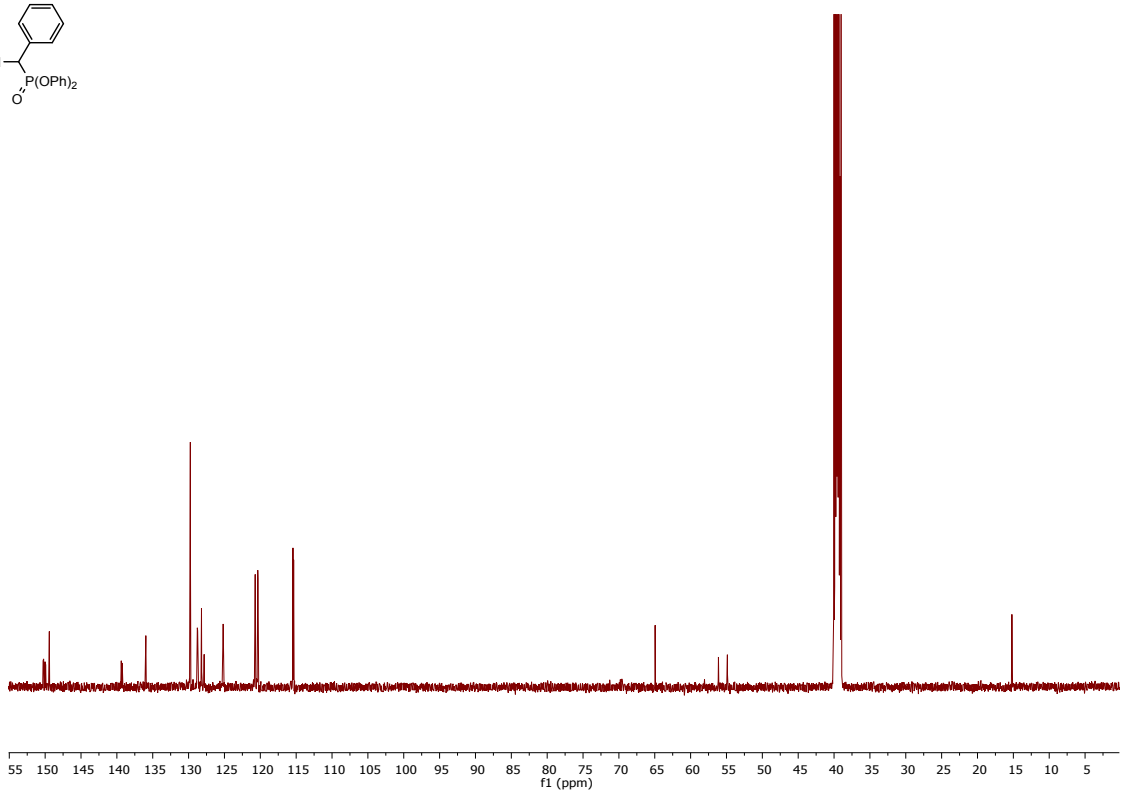
^{1}H NMR (500 MHz, DMSO-d_6) of tetraphenyl ((1,2-phenylenebis(azanediyl))bis(phenylmethylene))bis(phosphonate) **13**



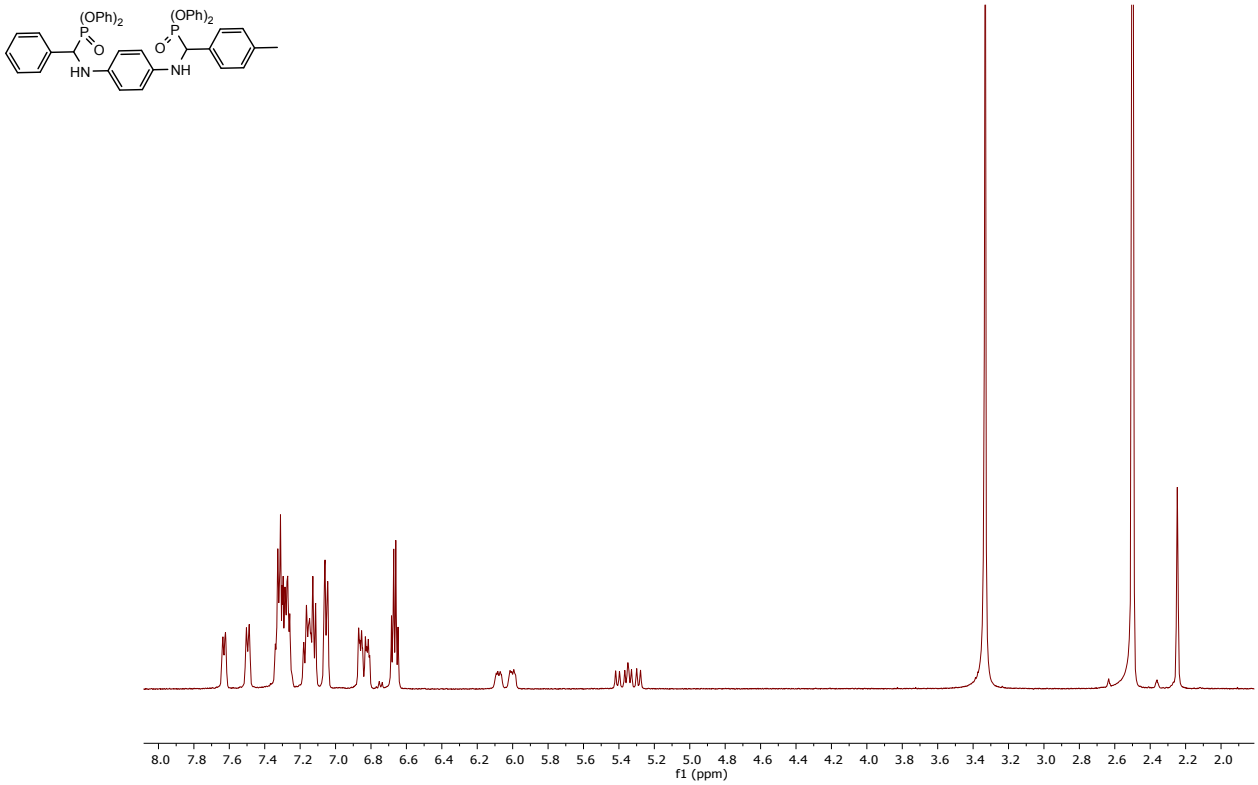


^{13}C NMR (126 MHz, DMSO-d_6) of tetraphenyl ((1,2-phenylenebis(azanediyl))bis(phenylmethylene))bis(phosphonate) **13**

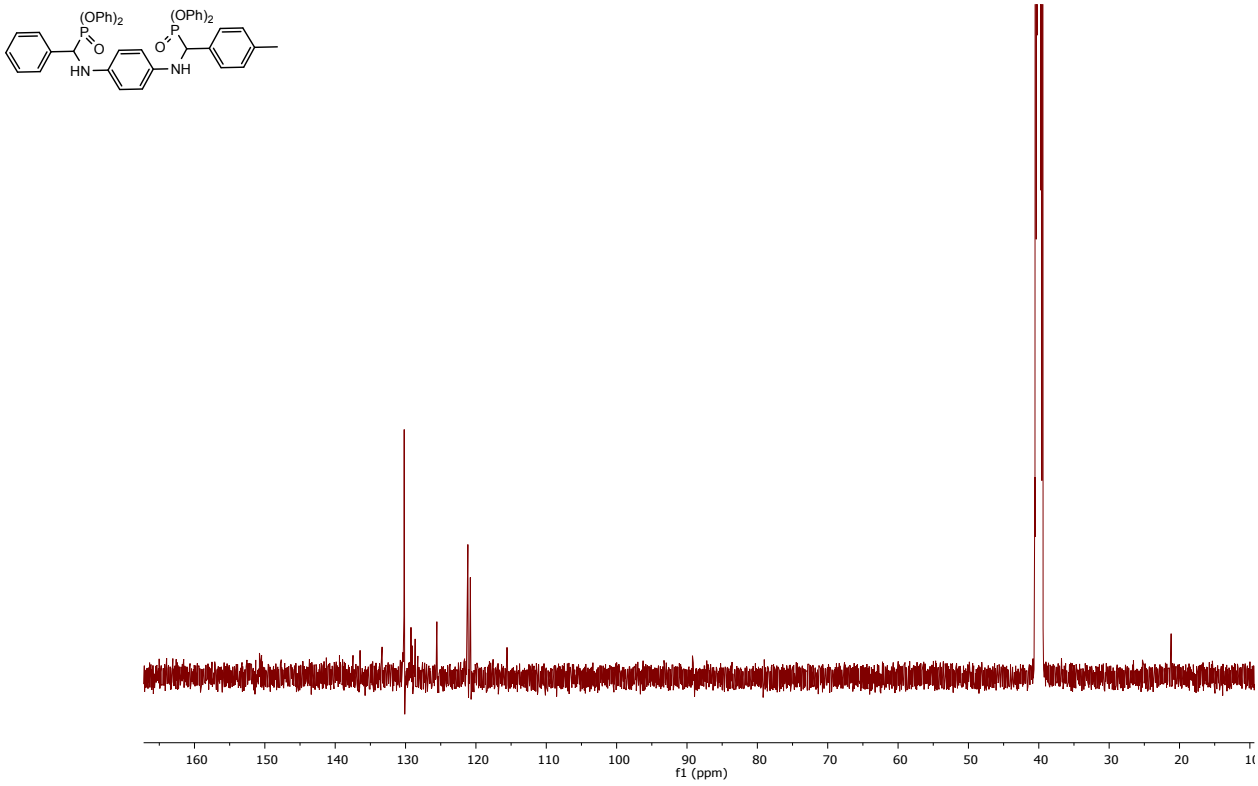




^{1}H NMR (500 MHz, DMSO-d_6) of diphenyl (((4-(((diphenoxyphosphoryl)(p-tolyl)methyl)amino)phenyl)amino)(phenyl)methyl)phosphonate **14**



^{13}C NMR (126 MHz, DMSO-d_6) of diphenyl (((4-(((diphenoxyphosphoryl)(p-tolyl)methyl)amino)phenyl)amino)(phenyl)methyl)phosphonate **14**



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